



## STRUCTURAL ELUCIDATION OF GLYCOSIDES FROM THE SEEDS OF *ENTADA PHASEOLOIDES* GROWING IN THUA THIEN HUE

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Received: 14 September 2018; Accepted for publication: 13 March 2019

**Abstract.** *Entada phaseoloides* (L.) Merr. belongs to Fabaceae family and is widely distributed throughout Viet Nam, Thailand, Malaysia, Indonesia, Philippines, China, New Guinea, and Australia. In Vietnamese traditional medicine, the seeds of *Entada phaseoloides* were used for the treatment of stomachache, haemorrhoids and hernia diseases. In this article, we report the isolation and structural elucidation of four glycosides from the water extract of seeds of *E. phaseoloides* including phaseoloideside C (**1**), phaseoloideside E (**2**), acanthoside D (**3**), and 1-(3,4,5-trimethoxyphenyl)prop-7-en-9-ol-O-(6''O- $\alpha$ -L-arabinopyranosyl)- $\beta$ -D-glucopyranoside (**4**). To the best of our knowledge, compounds **3-4** are isolated from *E. phaseoloides* for the first time.

**Keywords:** *Entada phaseoloides*, Fabaceae, saponin, phaseoloideside C, phaseoloideside E, and acanthoside D.

**Classification numbers:** 1.1.1; 1.1.6.

### 1. INTRODUCTION

*Entada* is a genus of the Fabaceae family comprising 30 species in the world and 3 species in Viet Nam (*Entada phaseoloides*, *Entada pursaetha*, and *Entada glandulosa*) [1, 2]. *Entada phaseoloides* is a woody climber distributed throughout Viet Nam, Thailand, Malaysia, Indonesia, Philippines, China, New Guinea, and Australia. The seeds of *E. phaseoloides* have been used as the folk medicine to treat stomachache, haemorrhoids, and hernia [2]. Pharmacological studies on extracts and isolated compounds from this plant displayed cytotoxic [1, 3], antidiabetic [4, 5], antioxidant [6, 7], antimicrobial [6, 8], antiviral [9] and anti-

inflammatory [10] activities. Besides, studies on chemical constituents of *E. phaseoloides* showed the presence of triterpenoid saponins [1, 3, 10-14], sulfur-containing amides [15-17], phenylacetic acid derivatives [9, 18] and flavonoids [8]. Herein, we reported the isolation and chemical structural elucidation of four glycosides from the seeds of *E. phaseoloides*.

## 2. MATERIAL AND METHODS

### 2.1. Plant Materials

The seeds of *E. phaseoloides* (L.) Merr. were collected in Nam Dong, Thua Thien Hue, Viet Nam, in August 2017 and identified by Dr. Vu Tien Chinh, Vietnam National Museum of Nature, VAST. A voucher specimen (MISR-2017-03) was deposited at MienTrung Institute for Scientific Research, VAST.

### 2.2. General experimental procedures

All NMR spectra were recorded on a Bruker AM500 FT-NMR spectrometer (500 MHz for  $^1\text{H}$ -NMR and 125 MHz for  $^{13}\text{C}$ -NMR). The HR-ESI-MS spectra were obtained using an AGILENT 6550 iFunnel Q-TOF LC/MS system. Plant sample was extracted on a JP. Selecta 300867 sonicator. Column chromatography was performed using a silica gel (Kieselgel 60, 70-230 mesh and 230-400 mesh, Merck) or RP-18 resins (150  $\mu\text{m}$ , Fuji Silysia Chemical Ltd.), thin layer chromatography (TLC) using a pre-coated silica-gel 60 F<sub>254</sub> (0.25 mm, Merck) and RP-18 F<sub>254S</sub> plates (0.25 mm, Merck).

### 2.3. Extraction and isolation

The seeds of *E. phaseoloides* (7.5 kg) were extracted with methanol (15 L x 3 times) under sonication at 50  $^{\circ}\text{C}$  for 3 h to give the methanol extract (EP, 850 g), which was then suspended in water (2 L) and partitioned with dichloromethane and ethyl acetate to yield dichloromethane (EPD, 50.0 g), ethyl acetate (EPE, 8.0 g), and water (EPW, 792.0 g) extracts. The water extract (EPW) was chromatographed on a Diaion HP-20P column and eluted with water to remove sugars and ionic compounds, then with increasing concentration of methanol in water (25 %, 50 %, 75 %, and 100 %) to yield four fractions, EPW1-EPW4, respectively. The EPW2 fraction was chromatographed on a silica gel column and eluted with mixtures of dichloromethane/methanol (20/1  $\rightarrow$  1/1, v/v) to yield five fractions, EPW2A- EPW2E. The EPW2C fraction was applied to a RP-18 column and eluted with acetone/water (1/2, v/v) to give two sub-fractions, EPW2C1-EPW2C2. Compound **1** (20 mg) was yielded by the purification of the EPW2C2 sub-fraction on a silica gel column using dichloromethane/methanol/water (2.5/1/0.1, v/v/v). The EPW2C1 sub-fraction was chromatographed on a silica gel column, eluted with dichloromethane/methanol/water (2/1/0.1, v/v/v) to obtain compound **2** (50.0 mg). The EPW2D fraction was separated by RP-18 column chromatography and eluted with methanol/water (1/2.5, v/v) to obtain three sub-fractions, EPW2D1-EPW2D3. The EPW2D1 sub-fraction continued to be chromatographed on silica gel column and eluted with dichloromethane/acetone/water (1/2.5/0.1, v/v/v) to yield compound **3** (8 mg). Finally, the EPW2D3 sub-fraction was further chromatographed on silica gel column and eluted with dichloromethane/acetone/water (1/2/0.1, v/v/v) to furnish compound **4** (6 mg).

**Phaseoloideside C (1):** White amorphous powder; HR-ESI-MS:  $m/z$  1544.7095  $[M+H]^+$  ( $C_{70}H_{113}NO_{36}$ ,  $M = 1544$ );  $^1H$ -NMR (500 MHz,  $CD_3OD-d_4$ ) and  $^{13}C$ -NMR (125 MHz,  $CD_3OD-d_4$ ) see Table 1.

**Phaseoloideside E (2):** White amorphous powder; HR-ESI-MS: 1586.7206  $[M+H]^+$  ( $C_{72}H_{115}NO_{37}$ ,  $M = 1586$ );  $^1H$ -NMR (500 MHz,  $CD_3OD-d_4$ ) and  $^{13}C$ -NMR (125 MHz,  $CD_3OD-d_4$ ) see Table 1.

**Acanthoside D (3):** White amorphous powder;  $^1H$ -NMR (500 MHz,  $CD_3OD-d_4$  in  $D_2O$ ),  $\delta$  (ppm): 6.76 (4H, s, H-2, 2', 6, 6'), 4.93 (2H, dd,  $J = 1.5, 7.0$  Hz, H-7, 7'), 3.27 (2H, m, H-8, 8'), 4.00 (2H, dd,  $J = 3.0, 8.5$  Hz, H<sub>a</sub>-9, H<sub>a</sub>-9'), 4.35 (2H, dd,  $J = 7.0, 8.5$  Hz, H<sub>b</sub>-9, H<sub>b</sub>-9'), 4.85 (2H, d,  $J = 9.0$ , Glc-H-1, 1'), 3.27 (2H, m, Glc-H-2, 2'), 3.49 (2H, m, Glc-H-3, 3'), 3.55 (2H, m, Glc-H-4, 4'), 3.52 (2H, m, Glc-H-5, 5'), 3.78 (2H, dd,  $J = 2.0, 12.0$  Hz, Glc-H<sub>a</sub>-6, 6'), 3.72 (2H, dd,  $J = 5.0, 12.0$  Hz, Glc-H<sub>b</sub>-6, 6'), 3.88 (12H, s, OCH<sub>3</sub>-3, 3', 5, 5');  $^{13}C$ -NMR (125 MHz,  $CD_3OD-d_4$  in  $D_2O$ ),  $\delta$  (ppm): 134.8 (C-1, 1'), 104.7 (C-2, 2', 6, 6'), 154.0 (C-3, 3', 5, 5'), 86.9 (C-7, 7'), 55.0 (C-8, 8'), 72.8 (C-9, 9'), 104.6 (Glc-C-1, 1'), 75.1 (Glc-C-2, 2'), 77.7 (Glc-C-3, 3'), 70.5 (Glc-C-4, 4'), 77.1 (Glc-C-5, 5'), 61.8 (Glc-C-6, 6'), 57.2 (OCH<sub>3</sub>-3, 3', 5, 5').

**1-(3,4,5-Trimethoxyphenyl)prop-7-en-9-ol-O-(6''-O- $\alpha$ -L-arabinopyranosyl)- $\beta$ -D-glucopyranoside (4):** Colourless oil;  $^1H$ -NMR (500 MHz,  $CD_3OD-d_4$ ),  $\delta$  (ppm): 6.76 (2H, s, H-2, 6), 6.65 (1H, d,  $J = 15.5$  Hz, H-7), 6.32 (1H, dt,  $J = 6.0, 15.5$  Hz, H-8), 4.34 (1H, dd,  $J = 6.0, 13.0$  Hz, H-9a), 4.51 (1H, dd,  $J = 6.0, 13.0$  Hz, H-9b), 4.39 (1H, d,  $J = 7.5$  Hz, H-1'), 3.28 (1H, dd,  $J = 7.5, 9.0$  Hz, H-2'), 3.33 (1H, m, H-3'), 3.82 (1H, m, H-4'), 3.38 (1H, m, H-5'), 4.13 (1H, dd,  $J = 2.0, 11.5$  Hz, H-6'a), 3.76 (1H, dd,  $J = 6.0, 11.5$  Hz, H-6'b), 4.36 (1H, d,  $J = 6.5$  Hz, H-1''), 3.48 (1H, m, H-2''), 3.54 (1H, m, H-3''), 3.90 (1H, m, H-4''), 3.63 (1H, m, H-5''a), 3.55 (1H, m, H-5''b), 3.87 (6H, s, OCH<sub>3</sub>-3, 5), 3.78 (3H, s, OCH<sub>3</sub>-4);  $^{13}C$ -NMR (125 MHz,  $CD_3OD-d_4$ ),  $\delta$  (ppm): 134.4 (C-1), 105.0 (C-2, 6), 154.6 (C-3, 5), 139.0 (C-4), 133.7 (C-7), 126.4 (C-8), 69.5 (C-9), 103.4 (C-1'), 75.1 (C-2'), 78.0 (C-3'), 71.7 (C-4'), 76.9 (C-5'), 69.4 (C-6'), 105.2 (C-1''), 72.4 (C-2''), 74.2 (C-3''), 70.8 (C-4''), 66.7 (C-5''), 56.7 (OCH<sub>3</sub>-3, 5), 61.2 (OCH<sub>3</sub>-4).

### 3. RESULTS AND DISCUSSION

Compound **1** was obtained as a white amorphous powder. Its molecular formula was determined as  $C_{70}H_{113}NO_{36}$  from pseudo-molecular ion peak at  $m/z$  1544.7095  $[M+H]^+$  (calcd. for  $C_{70}H_{114}NO_{36}$ , 1544.7121) in the HR-ESI-MS. The  $^1H$ -NMR spectrum of **1** observed signals of the protons of seven tertiary methyl groups at  $\delta_H$  0.77, 0.87, 0.90, 0.98, 0.99, 1.00, and 1.34 (each, 3H, s); a trisubstituted olefinic proton at  $\delta_H$  5.44 (1H, brs), and two oxymethine groups at  $\delta_H$  3.87 (1H, brs) and 4.33 (1H, brd,  $J = 3.0$  Hz), which suggested to be an entagenic acid aglycon [19, 20]. Besides, signals of seven anomeric protons were showed at  $\delta_H$  4.48 (1H, d,  $J = 8.0$  Hz), 4.49 (1H, d,  $J = 7.5$  Hz), 4.57 (1H, d,  $J = 6.5$  Hz), 4.65 (1H, d,  $J = 8.0$  Hz), 4.97 (1H, d,  $J = 3.0$  Hz), 5.37 (1H, d,  $J = 3.5$  Hz) and 5.43 (1H, d,  $J = 8.0$  Hz), suggesting the presence of seven sugar moieties. The  $^{13}C$ -NMR and DEPT of **1** showed the presence of 70 carbons including 2 carbonyls, 7 non-protonated, 36 methine, 17 methylene and 8 methyl carbons (Table 1). The signals of the carbonyl carbon ( $\delta_C$  173.2) and the methyl group ( $\delta_H$  1.96 (s),  $\delta_C$  23.2) in the HSQC spectrum suggested the presence of an acetyl group. The downfield chemical shift of C-3 ( $\delta_C$  91.1) and upfield chemical shift of C-28 ( $\delta_C$  176.8) were displayed in  $^{13}C$ -NMR spectrum, which suggested that compound **1** was a bidesmosidic glycoside of entagenic acid with two oligosaccharides linked at C-3 and C-28 [21]. Complete assignments of each sugar proton system were accomplished by analysis of  $^1H$ - $^1H$  COSY spectrum, while the carbons were

assigned from HSQC and HMBC spectra (Table 1). The coupling constant and chemical shift of the protons and carbons of the sugar moieties suggested the presence of one 2-(acetylamino)-2-deoxy- $\beta$ -glucopyranosyl (GlcNAc), one terminal  $\beta$ -glucopyranosyl (Glc1), one  $\alpha$ -arabinopyranosyl (Ara), one terminal  $\beta$ -xylopyranosyl (Xyl), one  $\beta$ -glucopyranosyl (Glc2), one  $\alpha$ -apiopyranosyl (Api1) and one terminal  $\alpha$ -apiopyranosyl (Api2) units (Figure 1). The sequence within the sugar chain at C-3 was determined by HMBC experiments. The key HMBC correlation between proton H-1 ( $\delta_{\text{H}}$  4.48) of GlcNAc and carbon C-3 ( $\delta_{\text{C}}$  91.1) of aglycon determined that the GlcNAc was linked to C-3 of aglycon (Figure 2). The important HMBC correlations between proton H-1 ( $\delta_{\text{H}}$  4.65) of Glc1 and carbon C-4 ( $\delta_{\text{C}}$  80.6) of GlcNAc, proton H-1 ( $\delta_{\text{H}}$  4.57) of Ara and carbon C-6 ( $\delta_{\text{C}}$  68.3) of GlcNAc, and between proton H-1 ( $\delta_{\text{H}}$  4.49) of Xyl and carbon C-3 ( $\delta_{\text{C}}$  83.1) of Ara showed the location of Glc1 at C-4 of GlcNAc, of Ara at C-6 of GlcNAc, and of Xyl at C-3 of Ara (Figure 2). In the same way, the other sugar chain at C-28 was determined by the key HMBC correlations of proton H-1 ( $\delta_{\text{H}}$  5.43) of Glc2 with carbon C-28 ( $\delta_{\text{C}}$  176.8) of aglycon, proton H-1 ( $\delta_{\text{H}}$  5.37) of Api1 with carbon C-2 ( $\delta_{\text{C}}$  79.9) of Glc2, and proton H-1 ( $\delta_{\text{H}}$  4.97) of Api2 with carbon C-5 ( $\delta_{\text{C}}$  71.4) of Api1 (Figure 2). Detailed analysis of HR-ESI-MS, 1D, 2D-NMR, and comparison with published data allowed us to determine compound **1** as phaseoloideside C [19].

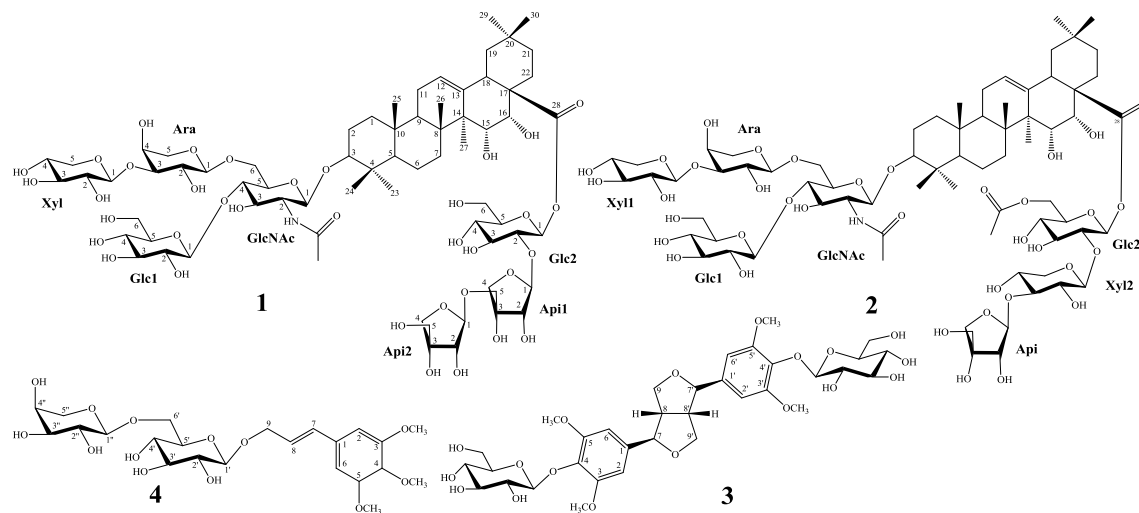


Figure 1. Chemical structures of compounds **1-4**.

Compound **2** was obtained as a white amorphous powder. Its molecular formula was determined as  $\text{C}_{72}\text{H}_{115}\text{NO}_{37}$  from pseudo-molecular ion peak at  $m/z$  1586.7206  $[\text{M}+\text{H}]^+$  (calcd. for  $\text{C}_{72}\text{H}_{116}\text{NO}_{37}$ , 1586.7226) in the HR-ESI-MS. Its  $^1\text{H}$ -NMR spectrum indicated the signals of nine methyl groups at  $\delta_{\text{H}}$  0.79, 0.83, 0.91, 0.96, 0.98, 1.03, 1.32, 1.96, and 2.07 (each, 3H, s), a trisubstituted olefinic proton at  $\delta_{\text{H}}$  5.40 (1H, brs), two oxymethine groups at  $\delta_{\text{H}}$  3.86 (1H, brs) and 4.33 (1H, brd,  $J = 3.5$  Hz), and seven anomeric protons at  $\delta_{\text{H}}$  4.48 (1H, d,  $J = 8.5$  Hz), 4.49 (1H, d,  $J = 7.5$  Hz), 4.57 (1H, d,  $J = 6.5$  Hz), 4.65 (1H, d,  $J = 8.0$  Hz), 4.69 (1H, d,  $J = 8.0$  Hz), 5.28 (1H, d,  $J = 3.0$  Hz) and 5.47 (1H, d,  $J = 7.5$  Hz). The  $^{13}\text{C}$ -NMR and DEPT of **2** displayed the signals of 72 carbons: 10 non-protonated (including 3 carbonyls), 37 methine, 16 methylene, and 9 methyl carbons (Table 1). The signals of two carbonyl carbons at  $\delta_{\text{C}}$  173.2, 172.7 and two methyl groups [ $\delta_{\text{H}}$  1.96 (s) and  $\delta_{\text{C}}$  23.2;  $\delta_{\text{H}}$  2.07 (s) and  $\delta_{\text{C}}$  20.8] in the HSQC spectrum suggested the presence of two acetyl groups. By comparing  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data, the structure of **2** can be similar with that of phaseoloideside C (**1**). However, the differences between them

are the component of sugar units of oligosaccharide chain at C-28 and an additional acetyl group. It was confirmed by the key HMBC correlations of proton H-1 ( $\delta_{\text{H}}$  5.47) of Glc2 with carbon C-28 ( $\delta_{\text{C}}$  176.9), proton H-1 ( $\delta_{\text{H}}$  4.69) of Xyl2 with carbon C-2 ( $\delta_{\text{C}}$  80.3) of Glc2, and proton H-1 ( $\delta_{\text{H}}$  5.28) of Api with carbon C-3 ( $\delta_{\text{C}}$  85.6) of Xyl2. Moreover, the HMBC correlation between proton H-6 ( $\delta_{\text{H}}$  4.20, 4.29) of Glc2 and acetyl group at  $\delta_{\text{C}}$  172.7 (C=O) showed the position of acetyl group at C-6 through an ester bond (Figure 2). All NMR assignments of **2** were confirmed by detailed analyses of HSQC and HMBC spectra, which are in good agreement with those reported in literature [11]. Consequently, compound **2** was identified as phaseoloideside E.

Similarly, detailed analysis of  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR data as well as comparison of them with the literature values led to the identification of compounds **3** and **4** as acanthoside D [22] and 1-(3,4,5-trimethoxyphenyl)prop-7-en-9-ol-*O*-(6''*O*- $\alpha$ -L-arabinopyranosyl)- $\beta$ -D-glucopyranoside [23].

Table 1. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data of **1-2** and reference compounds.

C	$\delta_{\text{C}}^{\#1}$	Compound 1		C	$\delta_{\text{C}}^{\#2}$	Compound 2	
		$\delta_{\text{C}}^{\text{a,b}}$	$\delta_{\text{H}}^{\text{a,c}}$ (mult., <i>J</i> in Hz)			$\delta_{\text{C}}^{\text{a,b}}$	$\delta_{\text{H}}^{\text{a,c}}$ (mult., <i>J</i> in Hz)
1	37.1	37.6	1.72 (m)	1	37.1	37.5	1.72 (m)
2	26.5	27.0	1.69 (m) 1.90 (m)	2	26.7	27.0	1.69 (m) 1.90 (m)
3	89.7	91.1	3.14 (dd, 4.0, 11.5)	3	89.7	91.1	3.14 (dd, 4.0, 11.5)
4	39.3	40.0	-	4	39.3	40.0	-
5	55.6	56.8	0.77 (m)	5	55.8	56.8	0.76 (m)
6	19.0	19.6	1.40 (m) 1.52 (m)	6	19.1	19.6	1.37 (m) 1.53 (m)
7	39.0	39.9	1.01 (m) 1.65 (m)	7	39.1	39.9	0.97* 1.63 (m)
8	42.1	42.2	-	8	41.6	42.2	-
9	47.5	48.3	1.54 (m)	9	47.5	48.3	1.54 (m)
10	37.2	38.0	-	10	37.1	38.0	-
11	24.1	24.7	1.92 (m)	11	24.1	24.7	1.88 (m)
12	124.8	125.8	5.44 (brs)	12	125.0	125.8	5.40 (brs)
13	144.7	144.9	-	13	144.6	144.8	-
14	47.9	48.5	-	14	47.7	48.5	-
15	68.9	69.3	3.87 (brs)	15	68.9	69.3	3.86 (brs)
16	79.1	79.5	4.33 (d, 3.0)	16	78.9	79.2	4.33 (brd, 3.5)
17	48.7	48.5	-	17	48.7	48.5	-
18	42.1	42.6	2.97 (dd, 4.0, 14.5)	18	41.9	42.5	3.02 (brd, 10.5)

19	46.7	47.4	1.02 (m) 2.32 (t, 13.5)	19	46.7	47.1	1.02 (m) 2.33 (t, 13.0)
20	30.9	31.3	-	20	30.9	31.4	-
21	36.0	36.5	1.19 (m) 1.97 (m)	21	36.3	36.5	1.18 (m) 1.98 (m)
22	31.9	32.0	1.92 (m)	22	31.7	32.3	1.84 (m) 1.97 (m)
23	28.2	28.6	0.98 (s)	23	28.1	28.6	0.98 (s)
24	17.1	17.1	0.77 (s)	24	17.1	17.1	0.79 (s)
25	15.8	16.2	0.99 (s)	25	15.8	16.3	0.96 (s)
26	18.1	18.3	0.87 (s)	26	18.1	18.5	0.83 (s)
27	20.8	20.5	1.34 (s)	27	20.8	20.5	1.32 (s)
28	175.7	176.8	-	28	176.1	176.9	-
29	33.4	33.4	0.90 (s)	29	33.4	33.4	0.91 (s)
30	24.6	24.8	1.00 (s)	30	24.5	24.9	1.03 (s)
<b>GlcNAc</b>				<b>GlcNAc</b>			
1	104.5	105.0	4.48 (d, 8.0)	1	104.6	105.0	4.48 (d, 8.5)
2	57.6	57.3	3.74 (m)	2	59.0	57.3	3.72 (m)
3	73.9	73.9	3.64 (dd, 8.5, 10.5)	3	73.9	73.9	3.64 (m)
4	81.0	80.6	4.04 (t-like, 8.0)	4	80.9	80.6	4.03 (m)
5	75.1	75.1	3.51 (m)	5	75.1	75.1	3.54 (m)
6	68.2	68.3	3.95 (m) 4.13 (m)	6	68.3	68.3	3.95 (m) 4.12 (dd, 6.0, 12.0)
CH <sub>3</sub> (Ac)	23.7	23.2	1.96 (s)	CH <sub>3</sub> (Ac)	23.8	23.2	1.96 (s)
C=O (Ac)	170.0	173.2	-	C=O	170.1	173.2	-
<b>Glc1</b>				<b>Glc1</b>			
1	104.5	104.3	4.65 (d, 8.0)	1	104.5	104.3	4.65 (d, 8.0)
2	74.8	74.9	3.32 (t-like, 8.0)	2	75.0	74.9	3.32 (m)
3	78.8	77.9	3.38 (m)	3	78.6	77.9	3.38 (m)
4	71.3	71.4	3.88 (m)	4	71.6	71.4	3.35 (m)
5	78.7	77.7	3.45 (m)	5	78.4	77.7	3.44 (m)
6	62.3	62.4	3.70 (m) 3.88 (m)	6	62.4	62.4	3.72 (m) 3.88 (m)
<b>Ara</b>				<b>Ara</b>			
1	103.5	103.6	4.57 (d, 6.5)	1	103.5	103.6	4.57 (d, 6.5)
2	73.2	73.9	3.74 (m)	2	73.2	73.9	3.74 (m)
3	83.4	83.1	3.76 (m)	3	83.9	83.1	3.75 (m)
4	68.5	71.1	3.38 (m)	4	68.9	71.1	3.39 (m)

5	66.4	66.5	3.54 (m) 3.87 (m)	5	66.4	66.5	3.55 (m) 3.87 (m)
<b>Xyl</b>				<b>Xyl1</b>			
1	107.0	107.6	4.49 (d, 7.5)	1	107.9	107.6	4.49 (d, 7.5)
2	76.7	76.4	3.28 (m)	2	74.8	76.4	3.28 (m)
3	78.9	78.0	3.38 (m)	3	78	78.0	3.38 (m)
4	71.0	71.1	3.50 (m)	4	70.8	70.8	3.50 (m)
5	67.5	67.4	3.28 (m) 3.88 (dd, 6.0, 11.5)	5	67.5	67.3	3.27 (m) 4.08 (dd, 6.0, 11.5)
<b>Glc2</b>				<b>Glc2</b>			
1	94.5	94.7	5.43 (d, 8.0)	1	93.3	93.6	5.47 (d, 7.5)
2	80.1	79.9	3.53 (m)	2	80.1	80.3	4.30 (brd, 10.5)
3	78.6	78.4	3.55 (m)	3	78.4	78.4	3.67 (m)
4	70.9	71.4	3.39 (t-like, 8.5)	4	70.4	69.8	3.37 (m)
5	78.2	78.4	3.33 (m)	5	78.2	78.4	3.64 (m)
6	62.5	62.4	3.70 (m) 3.80 (m)	6	64.2	64.5	4.20 (dd, 5.0, 12.0) 4.29 (brd, 10.5)
CH <sub>3</sub> (Ac)	-	-	-	CH <sub>3</sub> (Ac)	20.8	20.8	2.07 (s)
C=O (Ac)	-	-	-	C=O (Ac)	170.8	172.7	-
<b>Api1</b>				<b>Xyl2</b>			
1	110.9	110.9	5.37 (d, 3.5)	1	105.7	105.3	4.69 (d, 8.0)
2	78.0	78.7	4.00 (m)	2	75.9	75.9	3.43 (m)
3	80.4	80.4	-	3	85.0	85.6	3.41 (m)
4	75.2	75.2	3.78 (m) 4.11 (m)	4	69.5	69.0	3.56 (m)
5	71.6	71.4	3.55 (m) 3.75 (m)	5	67.2	66.9	3.20 (m) 3.96 (m)
<b>Api2</b>				<b>Api</b>			
1	110.8	110.8	4.97 (d, 3.0)	1	111.5	111.2	5.28 (d, 3.0)
2	77.6	77.9	3.93 (d, 3.0)	2	77.9	77.9	4.00 (d, 3.0)
3	80.4	80.4	-	3	80.5	80.5	-
4	75.1	75.2	3.78 (m) 4.00 (m)	4	75.2	75.3	3.62 (m)
5	65.5	65.5	3.60 (d, 2.0)	5	65.6	65.3	3.82 (m) 4.14 (m)

<sup>a</sup> measured in MeOD-d<sub>4</sub>, <sup>b</sup> 125 MHz, <sup>c</sup> 500 MHz, <sup>#1</sup>δ<sub>C</sub> of phaseoloideside C in pyridine-d<sub>5</sub> [19], <sup>#2</sup>δ<sub>C</sub> of phaseoloideside E [22]. \* Signal overlapped.

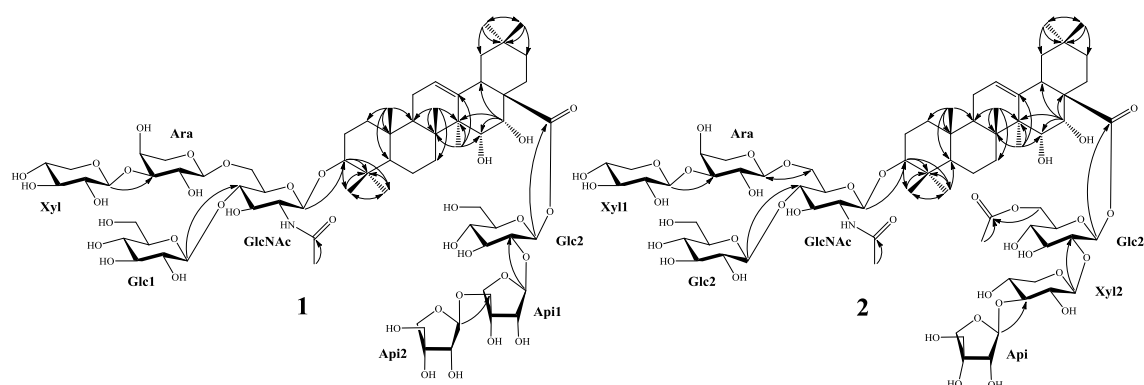


Figure 2. Key HMBC correlations of compounds **1-2**.

#### 4. CONCLUSIONS

The phytochemical study on the water extract of the seeds of *Entada phaseoloides* (L.) Merr. led to the isolation of four compounds including phaseoloideside C (**1**), phaseoloideside E (**2**), acanthoside D (**3**), and 1-(3,4,5-trimethoxyphenyl)prop-7-en-9-ol-*O*-(6''-*O*- $\alpha$ -L-arabinopyranosyl)- $\beta$ -D-glucopyranoside (**4**). Their chemical structures were elucidated by HR-ESI-MS data, 1D, 2D-NMR spectra analysis and in comparison with those reported in the literature. To the best of our knowledge, this is the first report of isolation of compounds **3-4** from this plant.

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